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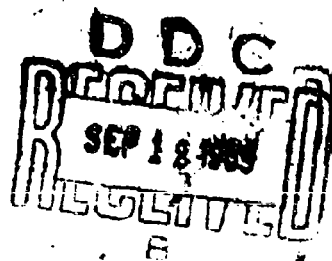
**THE INFLUENCE OF INITIAL TEMPERATURE ON THE LIMITS OF DETONABILITY**

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### Abstract

The influence of initial temperature ( $T_0 = 195^\circ\text{K}$  and  $T_0 = 295^\circ\text{K}$ ) on the limits of detonability of gaseous detonations is investigated for mixtures of  $\text{CH}_4 - \text{O}_2$ ,  $\text{H}_2 - \text{O}_2$ , and  $\text{H}_2 - \text{air}$  at one atmosphere initial pressure in long tubes of 4, 6, 10, 16 and 26 mm inner diameter, respectively, by use of a rotating drum camera. Two experimental designs are described to measure these limits at low initial temperatures. The regime of fuel gas concentrations for stable detonations becomes somewhat narrower at lower initial temperatures. The influence of the initial temperature on the critical tube diameter is estimated. Furthermore the applicability of the Chapman-Jouguet theory is discussed in relation to shock wave configurations, i.e. the Mach triple configuration. The essential arguments for the existence of the limits of detonability are discussed. Finally a new method to estimate the limits of detonability with a very simple experimental arrangement is des-

cribed. By this method experiments concerning the stability of a detonation and its initiation process are linked together.

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## LISTS OF ABBREVIATIONS AND SYMBOLS

D = detonation velocity

$M = \frac{D}{a}$  = Mach number

Q = heat of reaction per unit of mass

T = temperature

a = velocity of sound

c = concentration in Vol %

d = tube diameter

p = pressure

$\gamma$  = ratio of the specific heats

$\nu$  = frequency of spin

$\rho$  = density

Inde	CJ	refers to Chapman-Jouguet plane
	S	refers to values behind the front shock wave
	L	refers to the limits of detonability
	o	refers to the undisturbed fresh gas

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## I. INTRODUCTION

Shortly after the discovery of gaseous detonations by Bethelot and Vieille and by Mallard and Le Chatelier, Chapman and Jouguet gave a theoretical description of a one-dimensional detonation. Their theoretical model was very successful as far as the prediction of detonation velocities is concerned. The understanding of the stability of a detonation is not so well developed.

The stability of detonations is of interest in two respects.

- 1) Limits of detonability are the stability limits of selfsustained detonations. They are of great importance concerning the problems of safety.
- 2) The understanding of the stability of detonations is essential for the elucidation of the propagation mechanism of the detonation itself.

## II. THE ONE-DIMENSIONAL MODEL OF A DETONATION

In the classical model a detonation is described as

a shock wave behind which a rapid chemical reaction occurs after an induction time. Pressure, density, and temperature of the fresh gas are increased suddenly by the shock wave. During the induction time these values remain constant. But after the spontaneous onset of the exothermic chemical reaction the temperature increases, while the pressure and the density decrease to lower values. In this model a stable detonation can be described by the laws of conservation of mass, momentum, and energy. The Chapman-Jouguet law states, that for a stable detonation the Rayleigh-line has to touch the Hugoniot-curve for the final products. From this, it can be deduced that the velocity of a detonation is a minimum velocity. The basic assumption of this one-dimensional model is that a thermodynamic equilibrium exists both in front of and behind the reaction zone. However, the effects of transport phenomena, the influence of the tube diameter, the length of the reaction zone and the details of the chemical reaction were not considered. Detonation



velocities calculated by this model correlate with those obtained experimentally. However there exists sometimes a distinct discrepancy between calculated and measured values for the density and pressure.

### III. A DETONATION AS A THREE DIMENSIONAL PHENOMENON

Many experiments, using a variety of experimental techniques, have been performed to obtain a more realistic model of a detonation. Two ways are normally used for the experimental investigation of a detonation: the first is concerned with the macroscopic behaviour of a detonation and the second with the microscopic phenomena. The "microscopic" point of view is concerned mainly with the interaction of shock waves. Deep insight into the interaction of shock waves was obtained by the method of soot traces and instantaneous Schlieren photographs, especially by using Laser techniques [2]. Despite the great number of experiments and thorough theoretical calculations one is not yet able to give a theory describing a detonation as a whole

Especially the problems concerning the initiation of a detonation and the limits of detonability have not yet been solved. It is obvious, however, that a detonation is a three dimensional process with a very complex microscopic structure. The front of a stable detonation is uneven and determined by shock wave interactions, i.e. as the Mach triple configuration. Periodic movements of shock waves at the front of the detonation are coupled with transverse oscillations in the burnt gas as observed by the macroscopic phenomenon of spin. Transverse oscillations in the reaction zone seem to be responsible for the transport of energy to the detonation front, and a detonation is stable as long as these transverse oscillations are compatible with the boundary conditions.

#### IV. THE LIMITS OF DETONABILITY

In a plot of detonation velocity versus fuel gas concentration the limits of detonability are characterized by a jump in the detonation velocity. These limits

give the region of the gas mixture in which a stable detonation is possible. At the limits of detonability one always observes the lowest possible frequency of spin which can be calculated by a simple formula derived by Manson and Fay [3] .

$$v = \frac{1.84 \cdot a}{\pi \cdot d} \quad (\text{circular tube cross section})$$

Until now the influence of the tube diameter, the addition of inert gases to the explosive gas mixture, the initial pressure and temperature on the limits of detonability have been investigated [8] .

The principal results shall be summarized: the fuel gas concentration at the limits is a linear function of the reciprocal tube diameter for a wide range of tube diameters. The slope of this straight line is a measure of the influence of the tube diameter on the limits of detonability. The detonation velocity measured near the limits is in good agreement with the values calculated from the Chapman-Jouguet-theory. The addition of inert gases can lead to a detonation regime which is either smaller or larger than without an inert gas. This is mainly given by the ratio of

the specific heats behind the shock front and by the dilution of the reactive components of the gas mixture. A decrease in the initial pressure leads to a smaller detonation regime. As there exists a critical diameter for the propagation of a stable detonation, there also exists a critical pressure. This is the lowest pressure for which a stable detonation is possible.

#### V THE INFLUENCE OF INITIAL TEMPERATURE ON THE LIMITS OF DETONABILITY

Until now little is known about the influence of initial temperature on the limits of detonability, but the influence of initial temperature on the detonation velocity has been investigated several times [4]. Dixon measured the detonation velocities for mixtures of  $C_2H_4 + 2O_2$  and  $C_2N_2 + O_2$  at initial temperatures of 10 and 100 °C and at 1 atm. initial pressure. Laffitte investigated the detonation velocities of  $2H_2 + O_2$  (450 - 475 °C initial temperature) and

$\text{CH}_4 + 2\text{O}_2$  (525 - 530 °C initial temperature) at normal pressure. Ragland, Cosens, and Cullen determined detonation velocities of stoichiometric hydrogen-oxygen mixtures for low initial temperatures down to the vicinity of the oxygen vapour saturation point at initial pressures from 1 to 15 atm. Gordon and Zeleznik calculated detonation parameters of hydrogen-oxygen detonations from 0.01 to 100 atm initial pressure and from 200 to 500 °K initial temperature. Another investigation about the influence of initial temperature on detonations in hydrogen-oxygen has been published by Ladermann.

Summarizing all these investigations one can say: at constant initial temperature the detonation velocity increases with increasing initial pressure, and at constant initial pressure the detonation velocity decreases with increasing initial temperature. The variation in the detonation velocities is about 1 to 2 % when the initial temperature is varied by 100 °K. It should be mentioned that this result is in

accordance with the Chapman-Jouguet-theory.

The main subject of this report is the influence of initial temperature on the limits of detonability. What can be expected from the Chapman-Jouguet theory? If  $Q$  is the heat of reaction per unit mass,  $\kappa$  the ratio of the specific heats,  $D$  the detonation velocity,  $a$  the velocity of sound, and index  $o$  refers to the fresh gas, then the following relation holds approximately:

$$D^2 \approx 2 (\kappa^2 - 1) Q$$
$$T_{CJ} \approx \frac{T_o \kappa_o (\kappa_o - 1) D^2}{(\kappa_o + 1)^2 a_o^2}$$

In a first approximation the initial temperature  $T_o$  has no influence upon  $D$ .  $a_o^2$  is proportional to  $T_o$  and therefore the temperature at the CJ-plane,  $T_{CJ}$ , is approximately independent of  $T_o$ . From this it can be expected that a stable detonation should not be greatly influenced by the initial temperature. But at the limits of detonability the Chapman-Jouguet theory is not valid and here a greater influence of the initial temperature

can be expected.

## VI THE EXPERIMENTAL DESIGN

The influence of initial temperature on the limits of detonability was investigated at 1 atm. initial pressure and for initial temperatures of  $T_0 = 295^{\circ}\text{K}$  (room temperature),  $T_0 = 195^{\circ}\text{K}$  and  $T_0 = 135^{\circ}\text{K}$ .

The experiments were carried out for the following gaseous mixtures: hydrogen - oxygen, hydrogen - air, and methane - oxygen. For comparison with these initial temperatures, the boiling points of the components of the gaseous mixtures are given here:

Methane  $111.7^{\circ}\text{K}$

Oxygen  $90.2^{\circ}\text{K}$

Hydrogen  $20.7^{\circ}\text{K}$

Nitrogen  $77.4^{\circ}\text{K}$

### VI 1) THE PHOTOGRAPHIC TECHNIQUE

The combustion processes in the tubes were recorded by a rotating drum camera which is described in detail in [5]. With the film moving perpendicular

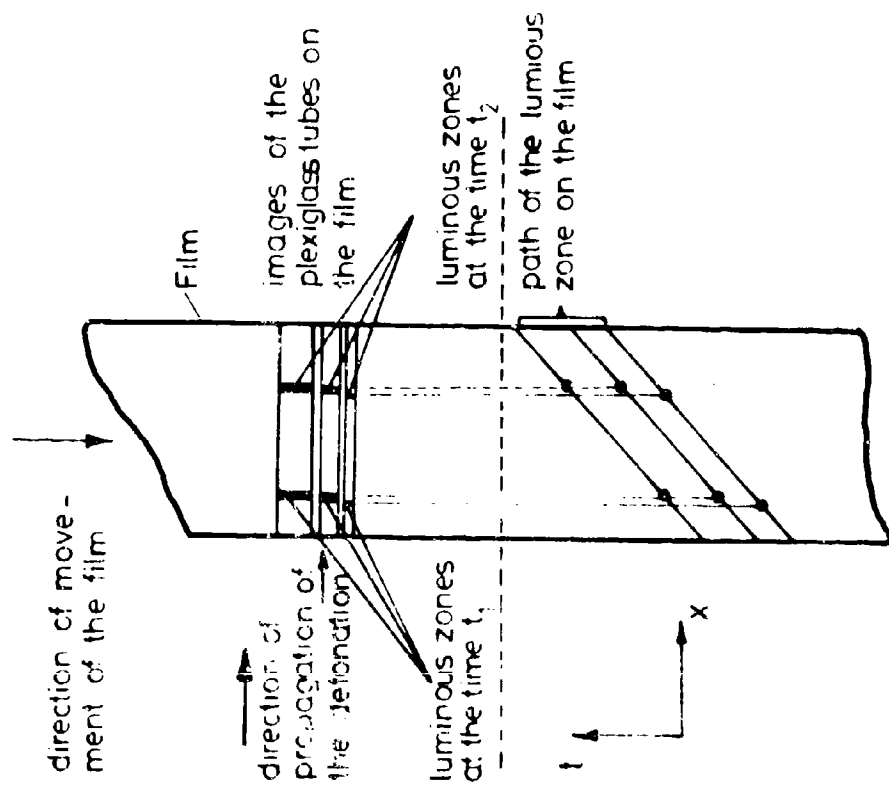


Fig. 1 Illustration of the formation of a space - time ( $x - t$ ) diagram on the film



to the image of <sup>the</sup> detonation front one obtains a space-time-diagram of the luminous zones of the combustion process. This luminous detonation front gives an inclined path on the film, and the slope of this path is dependent on the relative velocity of the film and the image of the luminous front. This is demonstrated schematically for a stable detonation in Fig. 1. The detonation velocity can be calculated from the slope of the path, the ratio of the original tube length to its image on the film, and the frequency of the rotating drum camera. This photographic investigation of the stability of a detonation has some advantage to the registration of the detonation velocity by an electric device. On the film not only the variation of the detonation velocity at the limit of detonability but also the structure of the combustion process is recorded. Studying the structure and the velocity of the detonation front one obtains a very critical proof of stability. From this point of

view a detonation is a stable detonation if the luminous path on the film is line and if its structure is regular (Picture 1). It is also understandable that there might be a slight difference in the results from this method to measurements made by the registration of the electrical signals of probes.

#### VI 2) THE DETERMINATION OF THE FUEL GAS CONCENTRATION

To avoid explosions hazards the explosive gas mixtures were not stored in tanks. The flowing gases were premixed roughly by means of flowmeters and the fuel-gas concentration was determined finally by a Zeiss Haber-Loewe-Gasinterferometer, which was thermostated at 24 °C. This interferometer was calibrated for each measurement with oxygen as reference gas. By this method the fuel gas concentration could easily be determined to an accuracy of  $\pm 0.5$  %. Commercial gases were used which were dried with a mixture of dry ice and methyl alcohol.

NOT REPRODUCIBLE



Picture 1: Two self-sustained detonations  
in  $H_2$  - air,  $T_0 = 295^\circ K$ ,  $p_0 = 1$  atm.

22, 1 Vol %  $H_2$

$d = 26$  two marks

$d = 16$  one mark

### VI 3) THE COOLING OF THE GASES

To cool down the explosive gas mixture it was necessary to use inflammable refrigerants. In the first step of the research the limits of detonability of methane-oxygen mixtures were investigated at  $T_0 = 295^\circ\text{K}$  and  $195^\circ\text{K}$ . This system is much easier to investigate than the other ones because of the higher luminosity of the detonation front. On the other hand the detonation pressures are expected to be higher than for  $\text{H}_2 - \text{O}_2$  mixtures. It was decided to use two experimental designs for cooling down the gases. The first experimental arrangement was a relative simple one and was used for  $T_0 = 195^\circ\text{K}$ . It was a 10 m long isolated container of aluminium in which the detonation tubes were cooled down with dry ice. For the heat insulation of the experiments at  $T_0 = 155^\circ\text{K}$ , a 7 m long cylindrical Dewar vessel was constructed and liquid nitrogen was used as a refrigerant. The Dewar was found to be more efficient at the lowest temperature because of its better insulating properties than that of the commercially

available materials. The thickness of the inner Dewar wall was as thin as possible to avoid too high a consumption of liquid nitrogen. This arrangement was found to be most satisfactory at lowest temperatures. For the experiments at  $T_0 = 195^\circ\text{K}$  the detonation tubes were constructed out of metal to which plexiglass tubes were connected.

Because at the lower initial temperature ( $T_0 = 135^\circ\text{K}$ ) the connections between the metal tubes and the plexiglass tube became loose, it was decided therefore to use plexiglass - XT throughout. No influence of the material of the tubes on the limits of detonability could be detected at room temperature.

#### VI 4) THE INITIATION OF THE DETONATION

The problem of cooling down the tubes gives an upper limit for the tube length. It was therefore decided to initiate the detonation in the test mixture using a stoichiometric mixture of the same components. However, the tubes must have a minimum length due to the existence

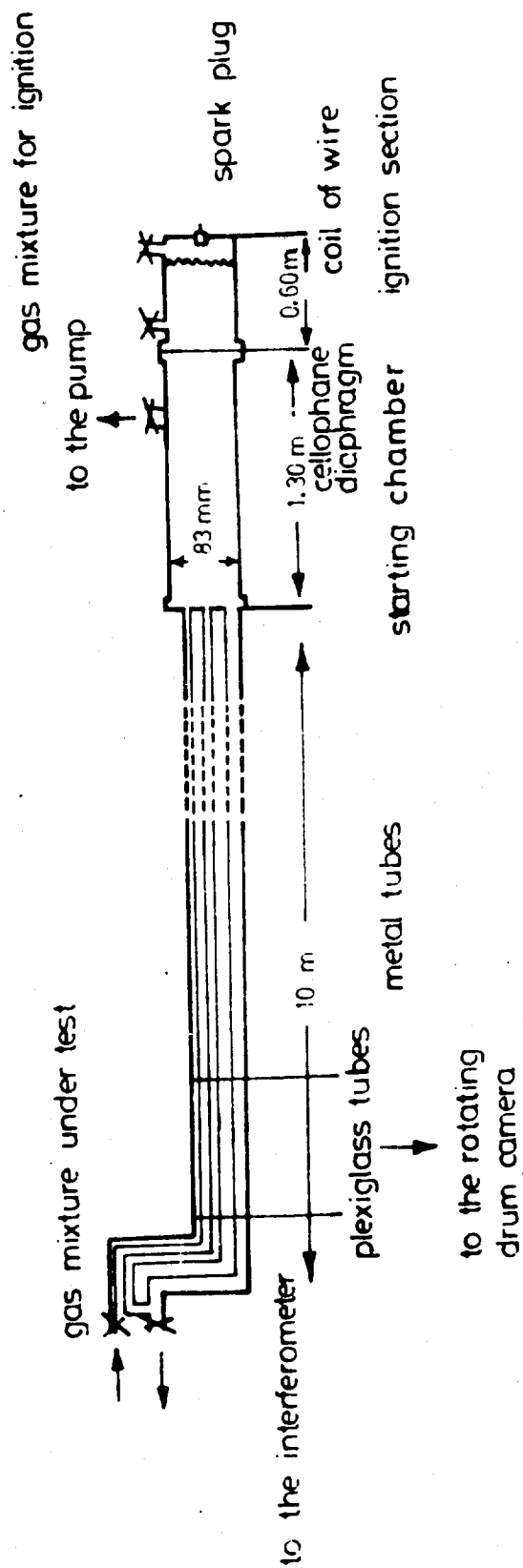


Fig. 2 Sketch of the Apparatus for  $T_0 = 195^\circ\text{K}$

of overdriven detonations in the first part of the tubes. For the  $H_2 - O_2$  and  $CH_4 - O_2$  systems tubes of 10 m length and an inner diameter less than 30 mm were found to be adequate. The general scheme of the experimental arrangement is illustrated in Fig. 2. In order to reduce the length of the ignition section a coil of wire was inserted [6]. This section was separated from the starting chamber by a diaphragm of cellophane or aluminium. In our case the kind of diaphragm did not influence the measurements.

#### VI 5) THE EXPERIMENTAL DESIGN FOR $T_0 = 195^\circ K$ AND THE DESCRIPTION OF MEASUREMENT

A sketch of the apparatus is given in Fig. 2. Each experiment was performed with three tubes of aluminium of 4, 6, 10, or 16, 26 mm inner diameter and 1 mm wall thickness. These tubes were situated one above the other with a distance of 1 cm between them. To get the length of the tubes of about 10 m, several tubes

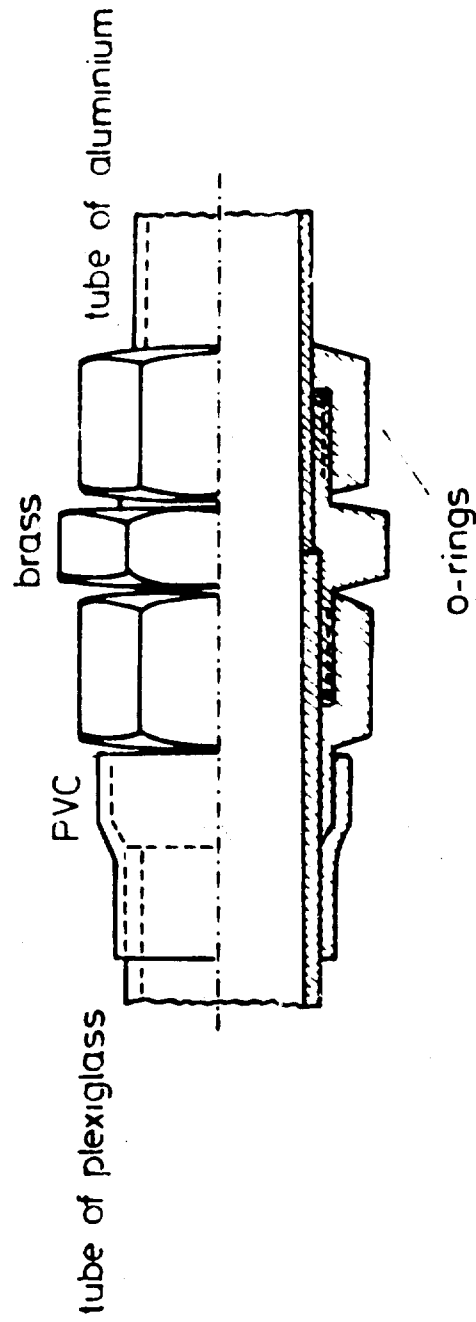


Fig. 3 Sketch of a Stuffing Box



of aluminium had to be joined with stuffing boxes and o-rings. The connection between the plexiglass tube and the metal tube was made in a same manner (Fig 3). It was taken care of the connections between two tubes to be smooth.

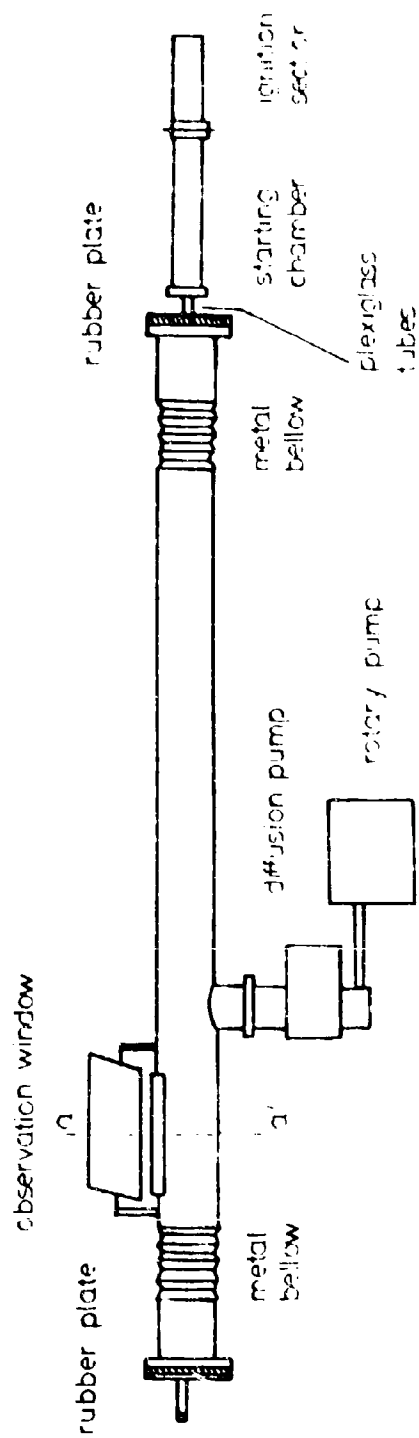
At the beginning of each experiment the tubes were put into the isolated container of aluminium with a cross section of 30 x 80 mm and 10 m length and the observation window at one end, which was normally closed by the isolating material (Eporit).

After the refrigerant of crushed dry ice was packed around the detonation tubes, the container was closed by plates of the isolating material. In this way the low temperature inside could be maintained without significant losses. The temperatures along the tubes were measured with thermocouples and monitored by a 12-point-recorder. After the tubes were cooled down to the temperature of dry ice, the premixed dried gases streamed through the smallest tube into the initiation section. From here the gases flowed through the two other tubes into a thermostated copper capillary which

led directly into the gas interferometer. From the interferometer the gas passed through a long PVC tube into the open air. The gas flow through the interferometer was about  $100 \text{ cm}^3/\text{sec}$ . If the reading remained constant for half an hour, the gas stream was stopped and the valves were closed. The composition of the mixture was then determined with the gas at rest. During the time while the gas in the tube was been cooled down to  $195^\circ \text{K}$ , the initiation section was filled. Prior to an experiment the isolating material was taken out of the window of the container and the outside of the plexiglass tubes was defrosted by methyl alcohol p.A.. The gas mixture in the initiation section was ignited by a spark plug and the detonations in the tubes were recorded by the rotating drum camera.

After each measurement the tubes had to be warmed up to room temperature and replaced if damage had been occurred.

# TOTAL VIEW



section a-a'

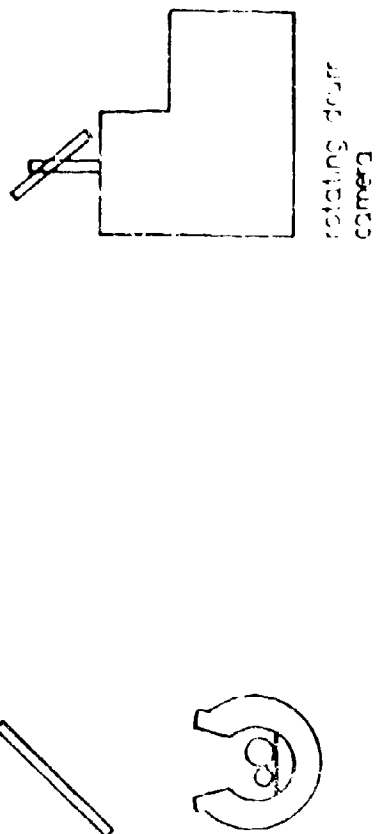


Fig. 4 Sketch of the Apparatus

The water inside was then removed by pumping. The dried tubes were then put back into the cooling system and a new experiment could be started.

It is interesting that at the low temperature at the limits of detonability dents were often observed along the first two or three meters of the aluminium tubes behind the starting chamber. There is no doubt, that this is an indication for the onset of detonations.

VI 6) THE EXPERIMENTAL DESIGN FOR  $T_0 = 135^\circ\text{K}$  (Fig. 4.4b)

For the experiments at this temperature plexiglass XT tubes of 7 m length with an inner diameter of 6, 10, 16, and 26 mm and a wall thickness of about 2 mm were used. To avoid too high a consumption of the refrigerant a 6.50 m long cylindrical Dewar vessel with a window of 60 cm length near one of its ends was constructed and built in our work shop. This Dewar was made of brass with an outer tube of 150 x 2.5 mm and an inner tube of 93 x

pg. 22

1.5 mm. The end plates of the Dewar vessel between the outer and the inner tube, and the frame of the window were made of German silver. The pressure in the Dewar vessel was kept at  $10^{-4}$  Torr with a rotary oil pump and an oil diffusion pump. For a Dewar vessel of this length the thermal dilatation must be compensated for. The inner part of the Dewar vessel was at 135 °K whereas the outer part was at room temperature and both parts were connected at the ends by German silver with 2 mm thickness. For this reason flexible metal bellows (Tombak) were soldered near both ends into the outer tube of the Dewar vessel. The window was built in a manner that it could overcome the resulting mechanical strains. Liquid nitrogen and  $\text{CF}_2\text{Cl}_2$  (F12) were used as refrigerants. The latter has a melting point at - 155 °C with a comparatively high heat of fusion. Thus an average temperature of  $- 140 \pm 5$  °C along the

straight tubes inside the Dewar vessel was achieved. At  $10^{-4}$  Torr in the Dewar vessel heat losses by conduction were kept to a minimum and those by radiation were reduced by polishing the inner surfaces of the Dewar vessel before mounting.

#### VI 7) DESCRIPTION OF MEASUREMENT AT 135 °K

In one experiment we only used two tubes lying side by side, which were filled with the gas under investigation in the manner described above. When the gas stream was stopped, both the valves were closed and the open ends of the plexiglass tubes were closed, too. The tubes were then inserted into the Dewar vessel which was already at the low temperature. The ends of the Dewar vessel were closed by placing rubber plates over them. These plates contained holes to enable the detonation tubes to pass through them (see Fig. 4). For cooling down of the tubes, a sufficient quantity of the refrigerant was then filled into the Dewar vessel. The pressure inside the closed detonation tubes was reduced at the lower temperatures.

In order to overcome this decrease of pressure, a flexible tube of PVC with a volume of approximately 10 l (inner diameter 16 cm) which acted as a gasometer was connected to the detonation tubes and filled with the same gas mixture. Thus the initial pressure in the system could always be maintained at 1 atm. by reducing the volume of this gasometer. In contrast to the apparatus described under 5) the two tubes for each experiment were situated side by side. A surface mirror located in front of the observation window was used to deflect the light of the detonations to the rotating drum camera.

After the cooling down of the tubes and the filling of the initiation section with the stoichiometric gas mixture, the insulating material in the observation window was removed and replaced by a plate of plexiglass to prevent heat convection and ice forming on the outside of the detonation tubes. The

detonations were then initiated and the subsequent combustion processes were recorded photographically. In both cases 5) and 7), the frequency of the rotating drum camera was measured by an oscilloscope, using Lissajous figures with a frequency generator as a standard.

After each measurement the tubes were taken out of the Dewar vessel, heated up to room temperature and the water inside was removed by pumping. It is to be mentioned that, at the limits of detonability, the plexiglass tubes were generally destroyed within a few meters after the starting chamber. This again was the point where the detonation was started.

#### VI 8) THE PHOTOGRAPHIC MATERIAL

It is known that for the gas systems under investigation the luminosity of the combustion processes near the limits of detonability is very weak. This is especially true for detonations in hydrogen - oxygen or hydrogen - air



mixtures were in the present investigation a lot of trouble was experienced in obtaining suitable photographs at the limits of detonability. Therefore extremely high speed panchromatic films i. e. Kodak 2475 Recording Film with DK 50 as a developer and Kodak High Speed Recording Film with MX 642-1 as a developer were used. The development was usually made at elevated temperatures. For detonations with higher luminosity Kodak TRI-X film with Kodak HC-110 developer was used.

#### VI 9) THE EVALUATION OF THE FILMS

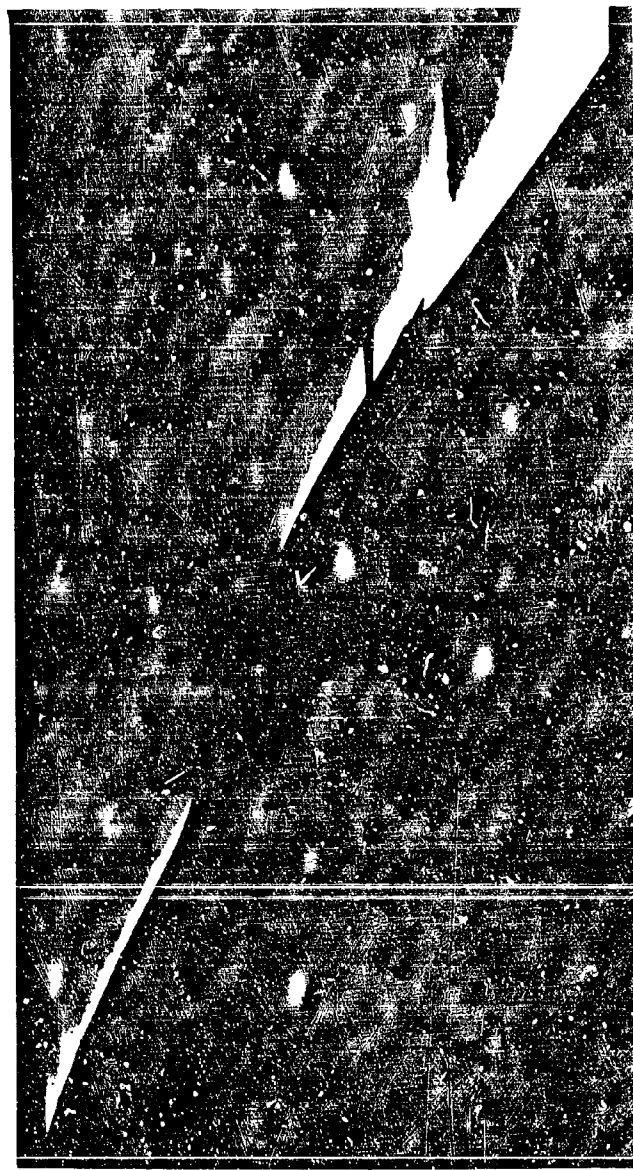
Depending of which experimental arrangement was used either two or three combustion processes were recorded (see Picture 1). If the detonation is a stable one, the path of the luminous detonation front has a very regular structure and can be approximated by a straight line. When the composition of the gaseous mixture approaches the value at the limit of detonability, the image of the detonation

NOT REPRODUCIBLE



Figure 2: A spinning detonation in  $H_2$  - air  
60.8 Vol %  $H_2$ ,  $T_0$  295 °K,  $p_0$  1 atm,  $d$  26mm

NOT REPRODUCIBLE



Picture 3: The onset of a detonation in  $\text{CH}_4 - \text{O}_2$

9,7 Vol %  $\text{CH}_4$ ,  $T_0 = 195^\circ\text{K}$ ,  $p_0 = 1 \text{ atm}$ ,  $d = 10 \text{ mm}$

front gradually changes into a sinusoidal form (see Picture 2). Beyond the limits of detonability one observes detonations dying off or starting with an alternating velocity of propagation. Finally only accelerated flames are recorded (Picture 3), which are much slower than detonations and which do not have such a marked structure, until nothing is to be seen on the film. Especially at the limits of detonability of hydrogen - oxygen mixtures a fairly wide range of detonative combustion beyond the limits of detonability was observed. This is a very important fact for safety purposes. Generally speaking as long as short sections are considered there is only a gradual change from the regime of a stable detonation to the regime of flames.

For the determination of the limits of detonability as a function of the tube diameter, the fuel gas concentration was first chosen such, that in at least one of the two or three tubes a stable detonation

could be expected. The limits of detonability for one tube diameter were determined by averaging between the two points having similar values of the fuel gas concentration, of which one belonged to a stable and the other to an instable detonation.

## VII EXPERIMENTAL RESULTS

### VII 1. DETONATION VELOCITY

The detonation velocity did not depend very strongly on the initial temperature. This is in good accordance with measurements discussed above. With an accuracy of measurement of about  $\pm 2\%$  we generally did not find any influence of the tube diameter on the detonation velocity. Only here and there just at the limits of detonability a very slight dependence of the tube diameter on the velocity of stable detonations was found. In Fig. 5 and 6 the Mach numbers for detonations

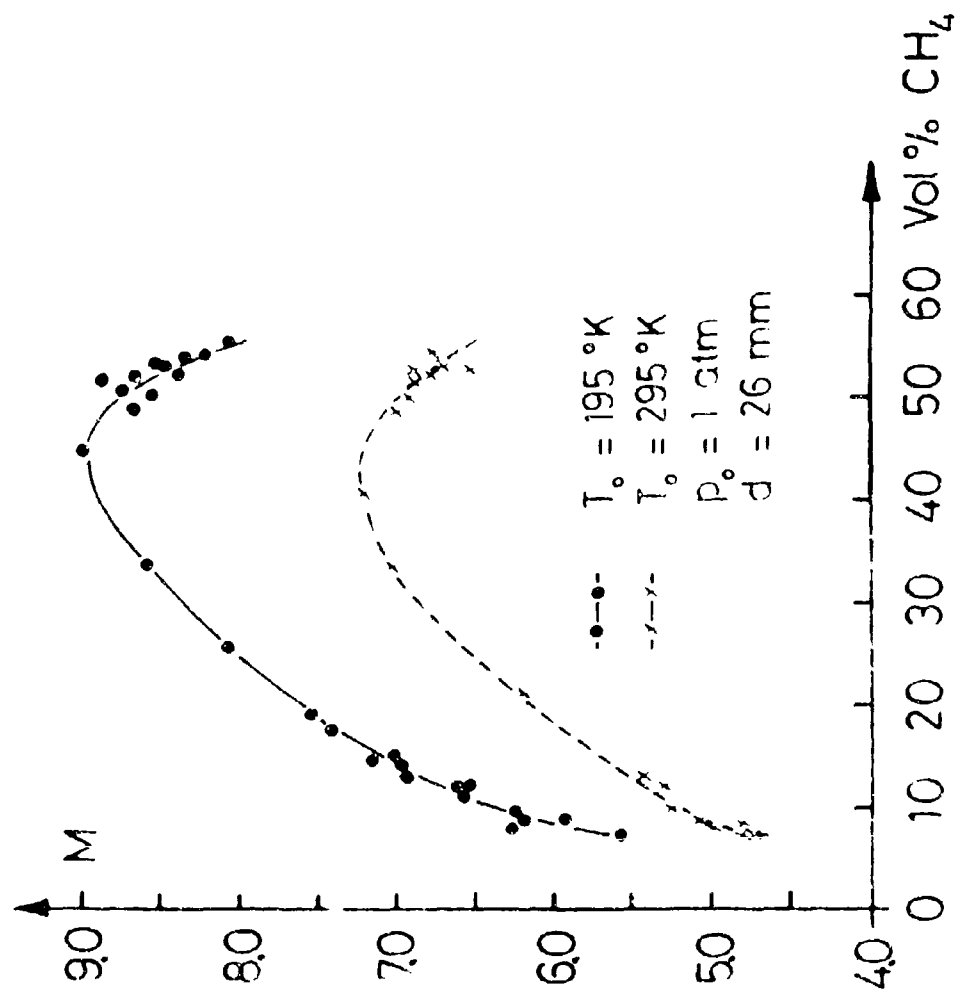


Fig. 5 Mach Number  $M = D/a_0$   
 $M = f(C_{\text{CH}_4})$

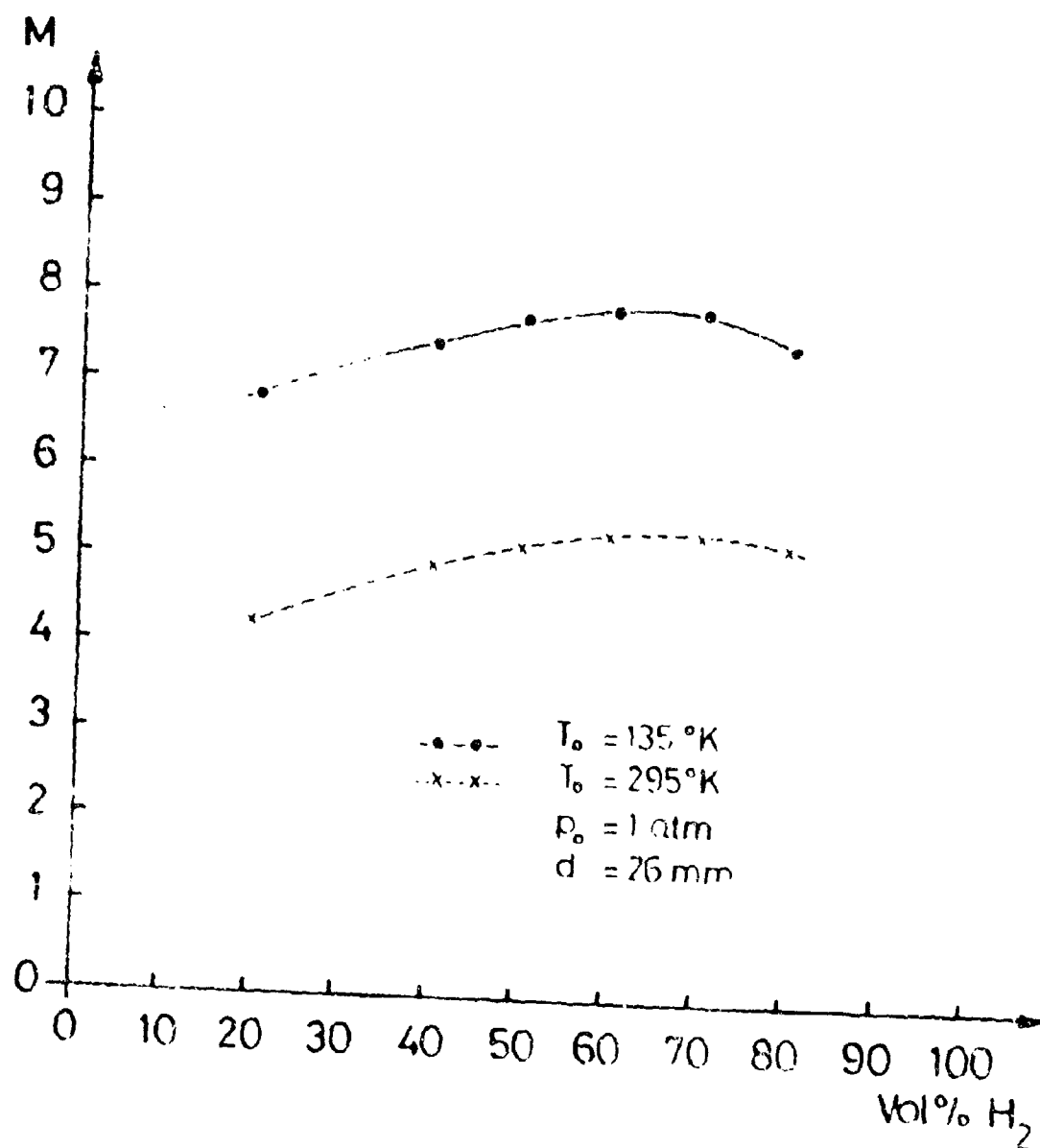


Fig. 6      Mach Number  $M = D/a_0$   
 $M = f(C_{\text{H}_2})$

in  $\text{CH}_4 - \text{O}_2$  and  $\text{H}_2 - \text{O}_2$  mixtures are plotted against fuel gas concentrations, with the initial temperature as a parameter. These Mach numbers determine the strength of the front shock waves. The Mach number is defined as the ratio of the detonation velocity and the velocity of sound in the unburnt gas.

#### VII 2. TEMPERATURE BEHIND THE SHOCK WAVE

With these measured detonation velocities the temperature behind the front shock wave was calculated for  $\text{CH}_4 - \text{O}_2$  (Fig. 7), assuming that just behind the shock wave there is no chemical reaction. The temperature behind the shock wave is nearly independent of the initial temperature. This temperature corresponds to the temperature at which the chemical reaction in the detonation zone first starts, assuming that the one-dimensional treatment of a detonation is valid. On the other hand the pressure behind the



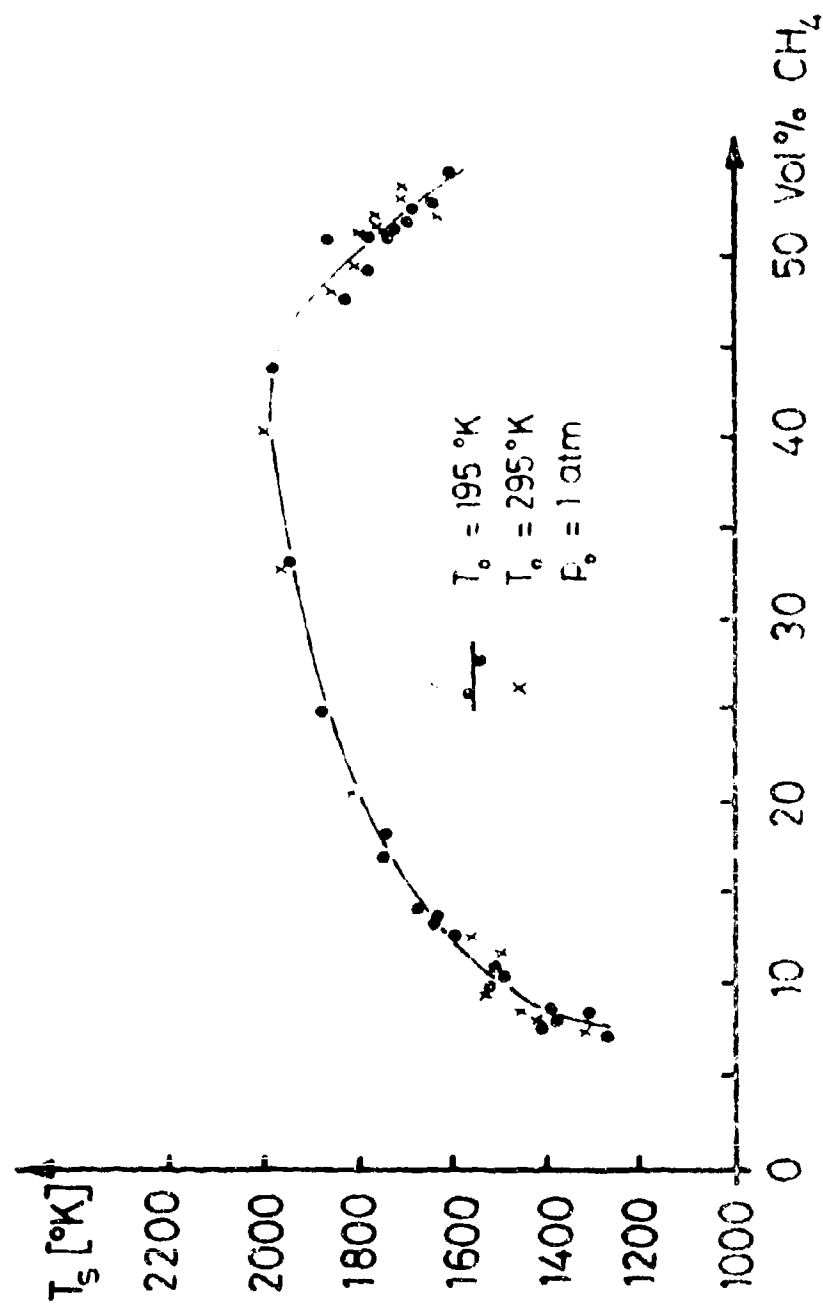


Fig. 7 Temperature behind the Front Shock Wave

shock wave is very strongly influenced by the initial temperature.

### VII 3. THE LIMITS OF DETONABILITY

The limits of detonability are represented in terms of fuel gas concentration as a function of the reciprocal tube diameter with the initial temperature as a parameter (Fig. 8, 9, 10). In these plots the upper and the lower limits of detonability are represented by straight lines, the slopes of which are a direct measure of the influence of the tube diameter. For all these systems under investigation the concentration regime of stable detonations becomes narrower for the lower initial temperatures. Also the influence of the tube diameter on the limits of detonability is a little more pronounced at the lower initial temperature. The measured values of the fuel gas concentrations at the limits of detonability are tabulated in Table 1. It must be pointed out that the values for

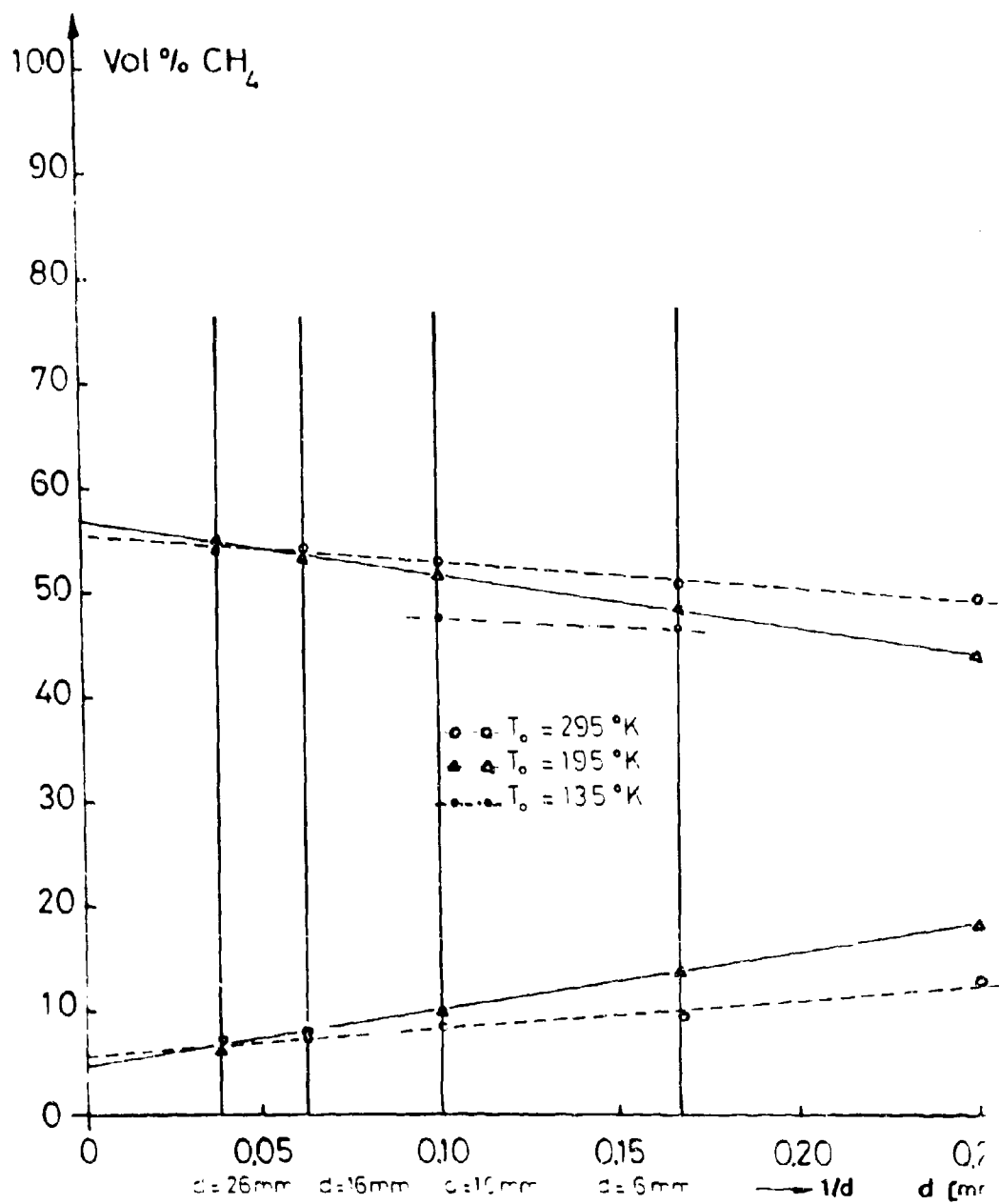
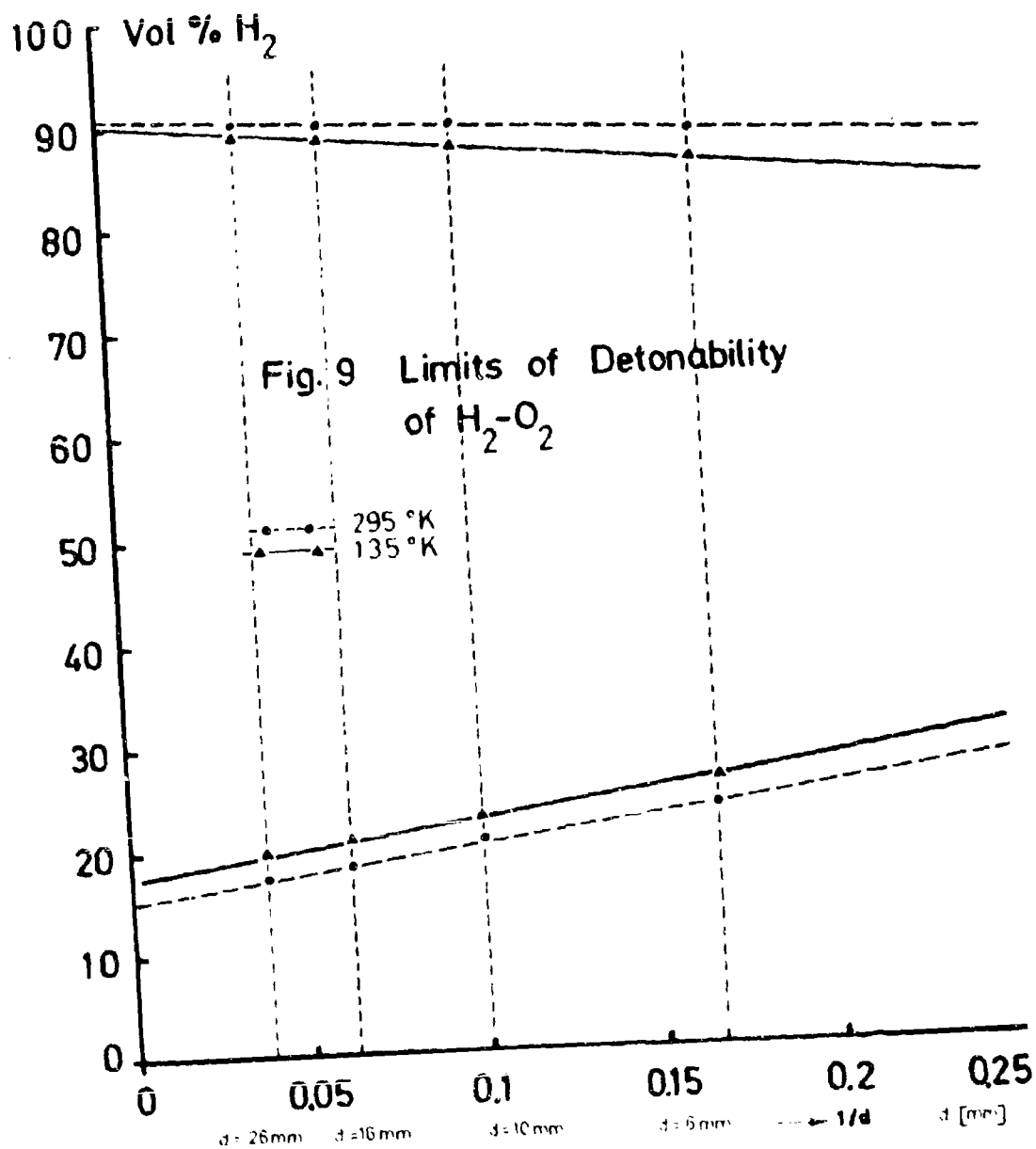


Fig. 8 Limits of Detonability of CH<sub>4</sub>-O<sub>2</sub>



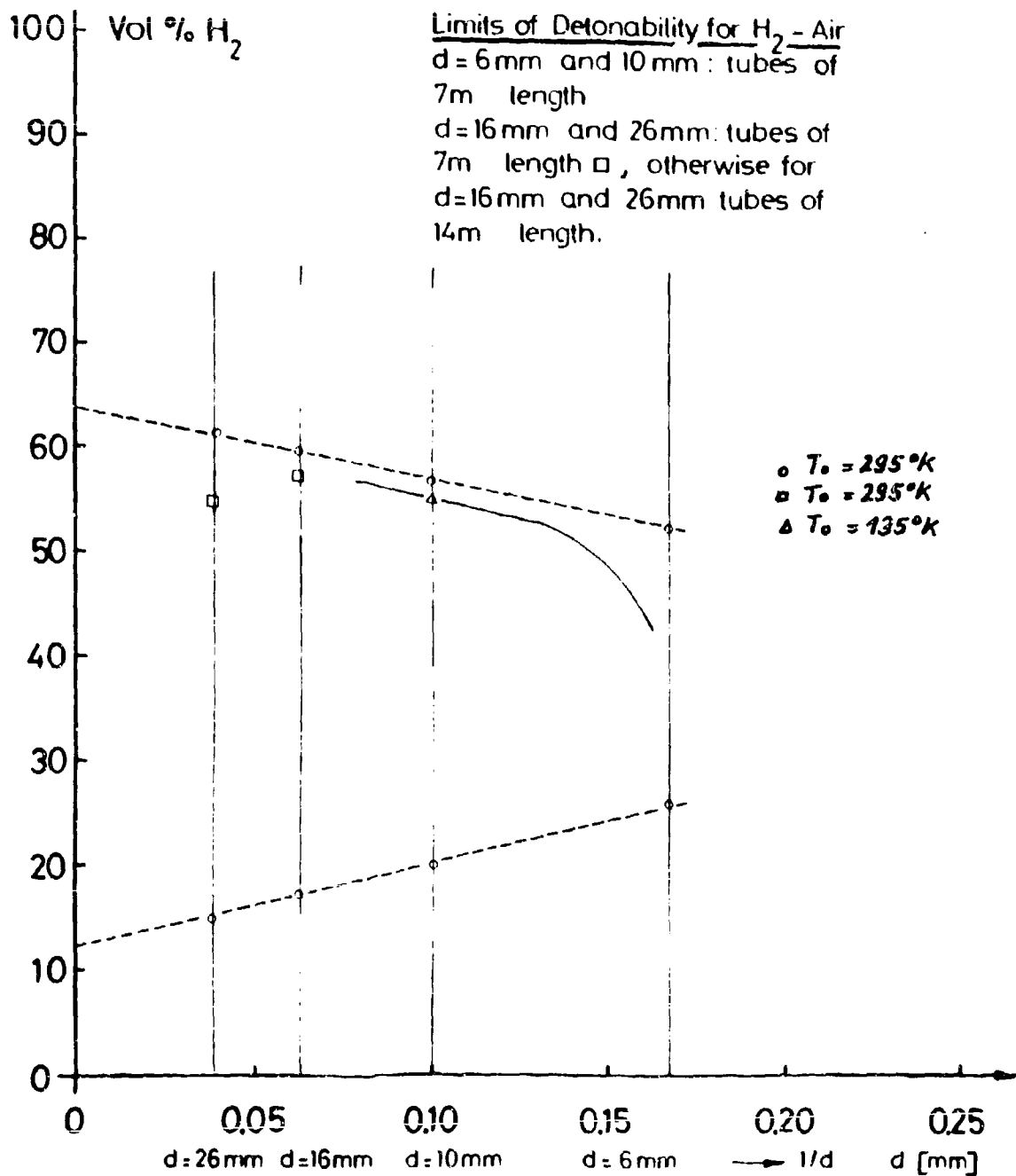


Fig. 10 Limits of Detonability for  $H_2$  - Air

Table 1 The measured limits of detonability

CH<sub>4</sub> - O<sub>2</sub>

T <sub>0</sub> [°K]	d [mm]	Vol % CH <sub>4</sub>	
		upper limit	lower limit
295	4	48.7	12.2
	6	50.7	10.0
	10	52.7	8.3
	16	53.6	7.3
	26	54.3	6.7
	∞	55.3	5.6
195	4	43.7	18.3
	6	48.0	13.7
	10	51.5	10.0
	16	53.4	8.0
	26	54.7	6.7
	∞	56.7	4.7
135	6	46.2	-
	10	47.3	-

H<sub>2</sub> - O<sub>2</sub>

T <sub>0</sub> [°K]	d [mm]	Vol % H <sub>2</sub>	
		upper limit	lower limit
295	6	87.9	23.3
	10	89.1	20.0
	16	89.7	18.3
	26	90.0	17.0
	∞	90.7	15.3
13	6	85.0	26.0
	10	87.3	22.7
	16	88.4	20.7
	26	89.0	19.6
	∞	90.4	17.5

Table 1

H<sub>2</sub> - air

$T_0 [^{\circ}\text{K}]$	length of the tube	$d [\text{mm}]$	Vol. % H <sub>2</sub>	
			upper limit	lower limit
295	7 m	6	52.6	25.8
	7 m	10	57.0	20.3
	14 m	16	59.4	17.3
	14 m	26	61.0	15.3
	7 m	16	57.3	-
	7 m	26	54.5	-
		$\infty$	63.6	12.4
135	7 m	10	55.1	-
	7 m	6	did not detonate	

$d \rightarrow \infty$  or  $1/d \rightarrow 0$  are extrapolated values and that they have no real physical significance. This can be seen very easily by the fact that detonations in tubes with very large inner diameters must be spherical detonations and these cannot be compared to detonations in tubes of small diameters.

For the system methane - oxygen only the upper limit of detonability for  $T_0 = 135^\circ\text{K}$  was measured for tubes of 10 and 6 mm inner diameter. This was done because the impact of the detonations was too high so that the Dewar vessel would have been damaged by more measurements.

The system hydrogen - air is a very interesting one. At room temperature the length of the tubes (7m) was insufficient for  $d = 16$  and 26 mm as can be seen in the plot. For this reason only the upper limit of detonability was investigated at  $T_0 = 135^\circ\text{K}$



for tube diameters of 6 and 10 mm. For  $d = 6$  mm and  $T_0 = 135^\circ\text{K}$  the gas mixture did not detonate.

To demonstrate the influence of initial temperature on a stable detonation some values just behind the shock front have been calculated for  $\text{CH}_4 - \text{O}_2$  at the limits of detonability (Table 2).

#### VII 4. THE CRITICAL TUBE DIAMETER

For tubes with an inner diameter less than the critical diameter a stable detonation is not possible. It is very difficult to measure this diameter directly, but from our measurements it can be estimated from Fig. 11, 12, 13. Thus the influence of the initial temperature on the critical tube diameter is obtained, and this will provide new informations for safety problems. The estimated critical tube diameters are shown in Table 3.

Table 2: Calculated values behind the front shock wave (the detonation velocity is measured)  
 $P_0 = 1 \text{ atm}$

$T_0 [^\circ K]$	$Vol\%CH_4$	$d [mm]$	$D [km/sec]$	$M=D/a_0$	$P_{st}/P_0$	$T_{st} [^\circ K]$	$T_{st}/T_0$	$\rho_{st}/\rho_0$	$p_{st}/p_0$	$\rho_{st} [10^{-3} g/cm^3]$
Lower limit:										
195	18.4	4	2.09	7.60	69.1	1760	9.0	7.7	14.2	
195	13.4	6	1.92	6.94	60.7	1630	8.4	7.3	13.6	
195	10.1	10	1.78	6.47	51.2	1490	7.7	6.6	11.6	
295	12.2	4	1.84	5.47	34.8	1620	5.5	6.3	7.8	
295	9.0	6	1.70	5.10	31.3	1470	5.0	6.3	8.0	
295	7.2	10	1.55	4.80	26.1	1300	4.4	5.9	7.5	
Upper limit:										
195	43.7	4	2.66	9.00	109.3	1990	10.2	10.7	16.7	
195	48.0	6	2.63	8.87	94.2	1900	9.7	9.7	14.7	
195	51.3	10	2.60	8.60	90.4	1760	9.0	10.0	14.9	
295	48.7	4	2.65	7.00	63.4	1380	6.4	9.9	9.9	
295	51.0	6	2.55	6.91	58.1	1170	6.0	9.1	9.0	
295	52.7	10	2.47	6.67	53.4	1690	5.7	9.3	9.1	

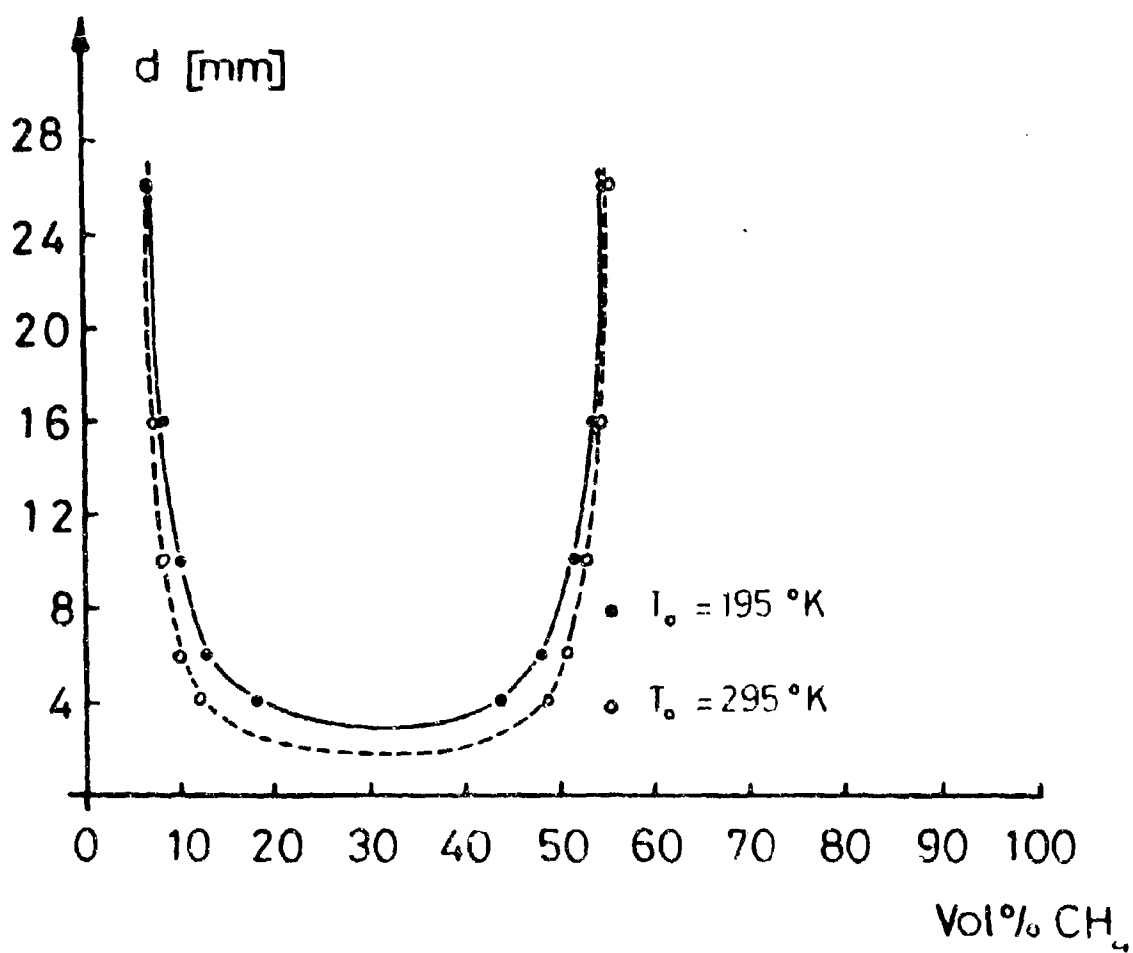


Fig. 11  $\text{CH}_4 - \text{O}_2$

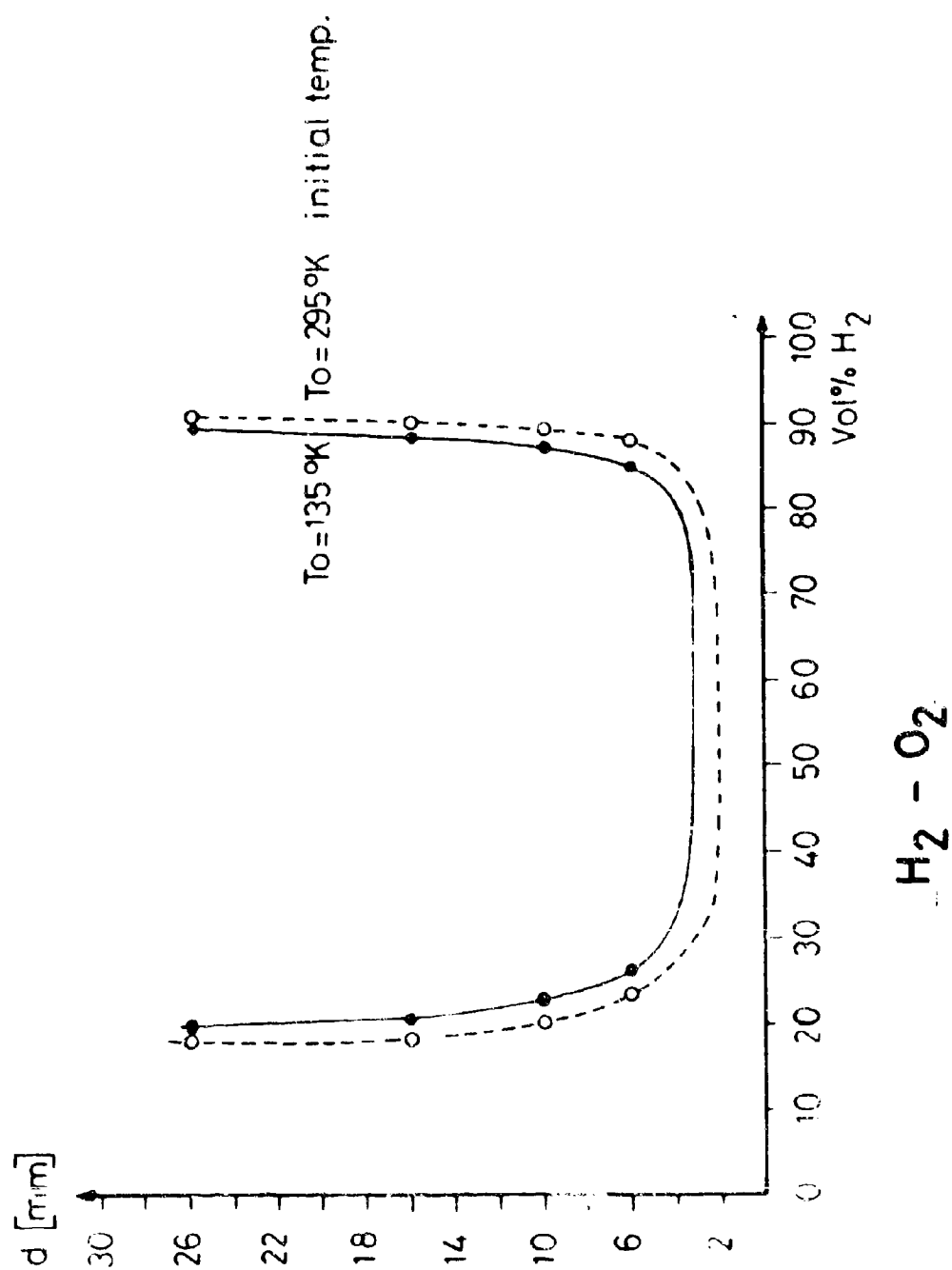


Fig. 12

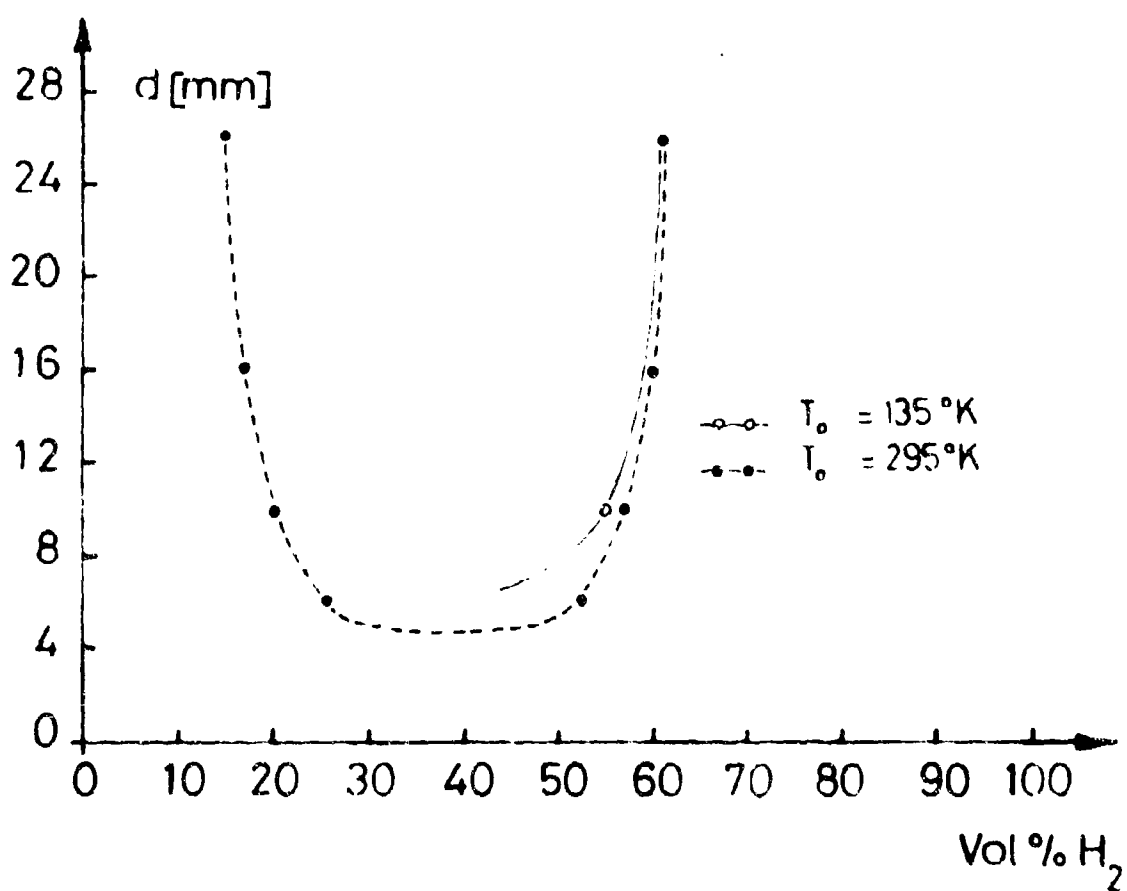
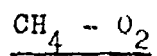


Fig. 13

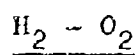
$\text{H}_2$  - air

Table 3: The extrapolated critical tube diameter



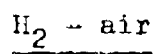
$T_o = 295 \text{ } ^\circ\text{K}$                        $d_{cr} \approx 2 \text{ mm}$

195  $^\circ\text{K}$                        $d_{cr} \approx 3 \text{ mm}$



$T_o = 295 \text{ } ^\circ\text{K}$                        $d_{cr} \approx 2 \text{ mm}$

135  $^\circ\text{K}$                        $d_{cr} \approx 3 \text{ mm}$



$T_o = 295 \text{ } ^\circ\text{K}$                        $d_{cr} \approx 6 \text{ mm}$

$T_o = 135 \text{ } ^\circ\text{K}$                        $d_{cr} \approx 5 \text{ mm}$

### VIII DISCUSSION

The classical hydrodynamic theory of a stable detonation is able to make good predictions concerning detonation velocities, pressures, and densities. The calculations for various initial temperatures give results which are in good agreement with the experimental values. In the case of a stable detonation the phenomenon of multiheaded spin occurs if the gas mixture is not too close to the limits of detonability. In this case the model of a one-dimensional shock wave, followed by a rapid chemical reaction, is a good approximation and it seems reasonable to consider a Chapman-Jouguet plane. This theory does not say anything about the limits of detonability. The existence of these limits can be attributed to phenomena which are not considered in this classical theory. These phenomena include reaction kinetics, hydrodynamic perturbations, and the coupling of transversal shock waves with

the possible acoustic oscillations in the burnt gases given by the boundary conditions. From the point of view of the reaction kinetics one has to consider the heat release by the exothermic chemical reaction and the time for the heat release, because this is the energy source for the front shock wave. If these waves are to influence the stability of a detonation, the interaction of waves must be considered between the shock wave at the front and the place where the local Mach number reaches the value one. This follows from the Chapman-Jouguet theory. All these phenomena cannot be considered separately, and this is the cause for the complex nature of a detonation and the difficulty involved in explaining the existence of the limits of detonability. At the limits of detonability one always observes single headed spin. The detonation front is given by a shock wave configuration like the Mach triple configuration. Furthermore there is a measurable local separation of the shock wave at the



front of the reaction zone. The fact, that at the limits of detonability the ratio of the wave length of the acoustic oscillation in the burnt gases to the tube diameter always reaches a critical value, indicates a coupling of the shock waves at the front with these acoustic oscillations.

From these facts one can try to explain the influence of initial temperature on the limits of detonability. Why do these limits become narrower for lower initial temperature ? We have seen that the temperature behind the shock wave at the detonation front is almost independent of initial temperature, and this temperature is determinative for the chemical reaction. From this point of view the reaction could only be influenced by the higher pressure behind the shock wave at the lower initial temperature. Because the reaction time is proportional to  $p^{-n}$  this might prove to have a slight influence. But then the detonation limits would become wider with lower initial temperature .

There must be a dominant effect into the other direction. Investigations of detonation spin with the film moving in the direction of the detonation front with the same velocity demonstrated, that also at low temperatures there is a periodically moving luminous zone in the detonation front. This luminous zone is the zone of strong chemical reaction. This picture of an oscillating zone of strong chemical reaction in the detonation front is supported by the reaction zone behind a triple Mach configuration as demonstrated by Edwards a.o. [7] . At the limits of detonability one triple Mach configuration goes to and fro between the walls of the tube, and the zone of the strongest chemical reaction also oscillates. If the reaction zone is near the wall of the tube, it might be influenced by the cool boundary layer, and for this reason the lower initial temperature might lead to a narrower detonation regime. Another possibility as to why the lowering of the initial

temperature reduces the stability of a detonation is the existence of rarefaction waves coming from the cold wall into the zone between the front shock waves and the regime of Mach number one. This should be possible at the limits of detonability because of the greater separation of the front shock waves and the Chapman-Jouguet plane. Furthermore the damping of the acoustic waves in the burnt gases must also be considered.

Only the influence of low initial temperatures on the limits of detonability has been investigated. What will happen if the initial temperature is increased? There is one critical case. If the initial temperature reaches the value for the self-ignition of the detonative gas mixture, no detonation can be generated anymore. In a similar manner, the onset of a detonation from a laminar burning flame is restrained by higher initial temperatures. Thus the detonation regime might

be expected to become narrower for higher initial temperatures. Then there should be a range of temperature at which the detonation regime reaches a maximum.

#### IX A METHOD TO APPROXIMATE THE LIMITS OF DETONABILITY

For a stable detonation the detonation velocity is independent of the length of the tube and therefore independent of the kind of ignition, provided that the ignition was strong enough to ignite the gases. Therefore one should expect, that the limits of detonability in very long tubes are independent of the manner of igniting either by an initial detonation or by a weak flame. To test this, we took a tube of plexiglass of about 3 m length with one end closed. Near the closed end the detonative gas mixture was ignited by a pilot flame through a small hole in the wall of the tube. By this weak ignition no shock waves were produced at the point of ignition. The induction time and the induction distance were measured from the point of ignition to the point of the onset of the

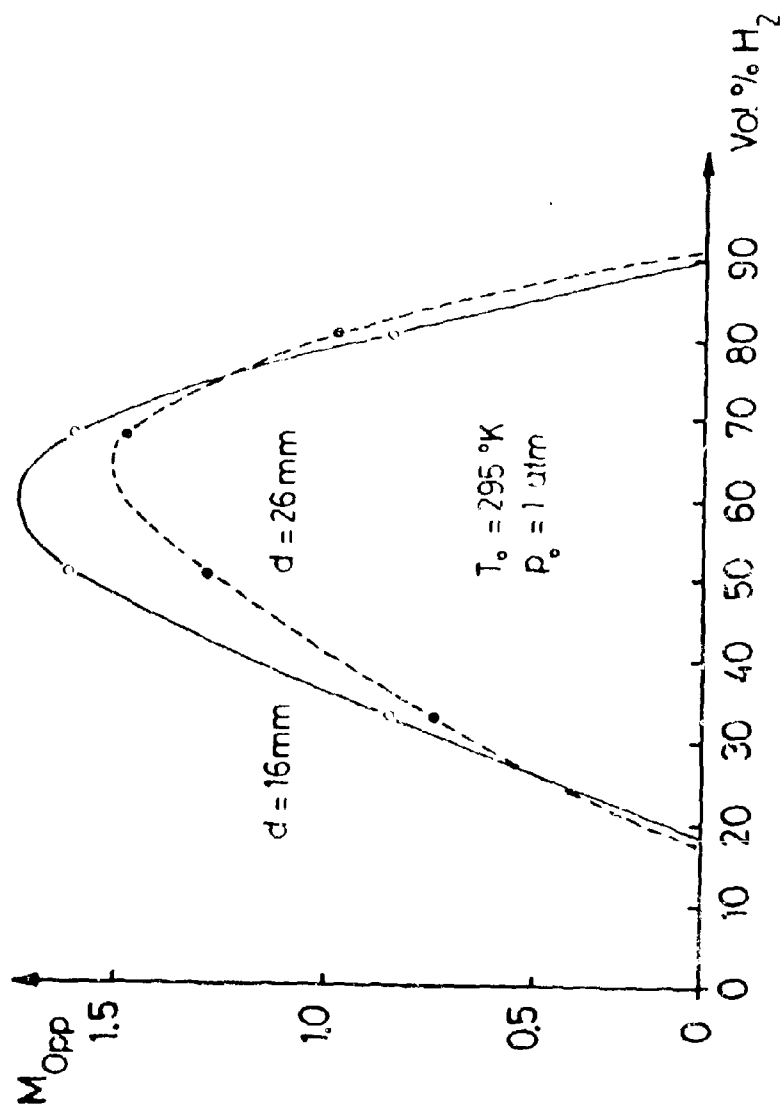


Fig. 14  $M_{Opp} = f(C_{H_2})$

detonation which is indicated by a high luminosity and the occurrence of the detonation wave. The ratio of the initiation distance over the initiation time, the Oppenheim velocity, divided by the velocity of sound of the undisturbed gas was plotted against the fuel gas concentration (Fig. 14). The extrapolation of these curves to  $M_{Opp} = \frac{V_{Opp}}{a_0} \rightarrow 0$  gives the limits of detonability, measured in long tubes of the same diameter with the experimental designs described above. This approach is a very simple one to determine the limits of detonability. It is at least a very good method to estimate the limits of detonability, which can otherwise only be measured with great experimental expenditure.

REFERENCES

- [1] H. Gg. Wagner: "Gaseous Detonations and the Structure of a Detonation Zone" in Fundamental Data Obtained from Shock Tube Experiments, Editor: A. Ferri. Pergamon Press, 1961
- [2] W. E. Gordon, A. J. Mooradian, S. A. Harper: "Limit and Spin Effects in Hydrogen - Oxygen Detonations". Seventh Symposium (International) on Combustion. Butterworths Scientific Publications, London, (1959), 752
- Yu. N. Denisov, Ya. K. Troshin: "On the Mechanism of Detonative Combustion"; Eighth Symposium (International) on Combustion, (1962), 600
- K. I. Shchelkin: "Two Cases of Unstable Combustion"; J. Expt. Theoret. Phys. (USSR), 36, (1959), 600  
engl. in : Soviet Phys. JETP 9, 416
- K. I. Shchelkin, Ya. K. Troshin: "Non Stationary Phenomena in the Gaseous Detonation Front"; Comb. Flame 7, (1963) 143
- G. L. Schott: "Observation of the Structure of Spinning Detonation"; Phys. Fluids 8, (1965), 850
- R. I. Soloukhin: "Multiheaded Structure of Gaseous Detonation"; Comb. Flame 10, (1966)
- D. H. Edwards, D. J. Parry, A. I. Jones: "On the Coupling Between Spinning Detonation and Oscillations behind the Wave"; British J. Appl. Phys. 17, (1966), 1507
- D. H. Edwards, D. J. Parry: "Wave Front Structure in Spinning Detonation"; J. Fluid Mechanics 26, (1966), 321

- P. A. Urtiew, A. K. Oppenheim: "Experimental Observations of the Transition to Detonation in an Explosive Gas"; Proceed. Royal Soc. (London), A 295, (1966), 13
- R. A. Strehlow: "Gas Phase Detonations: Recent Developments"; Comb. Flame, 12, (1968), 81
- [3] N. Manson: "Propagation des détonations et des déflagrations dans les mélanges gazeux". Paris 1947
- J. A. Fay: "A Mechanical Theory of Spinning Detonation"; J. Chem. Phys. 20, (1952), 942
- [4] H. B. Dixon: Phil. Trans. A 184, (1893), 97  
200, (1903), 315  
 Trans. Chem. Soc. 759, (1896)  
 Trans. Faraday Soc. 22, (1926), 372
- L. Laffitte: "Recherches expérimentales sur l'onde explosive et l'onde de choc"; Annales de physique, X<sub>3,4</sub>, (1925), 586
- K. W. Ragland, G. L. Gosens, R. E. Cullen: "Detonation of Hydrogen - Oxygen at Low Temperature and High Pressure"; AIAA J. 2, (1964), 142
- F. J. Zeleznik, S. Gordon: "Calculation of Detonation Properties and Effect of Independent Parameters on Gaseous Detonation"; ARS J. 32, (1962), 606
- A. J. Ladermann: Final Report on Contract NAS 8-2634, Series No. 6, Issue No. 11, April 1965



- [14] J. P. Toennies, H. Gg. Wagner: "Photographische Untersuchungen an spinnenden Kohlenoxyd-Sauerstoff-Detonationen" Z. Elektrochem. 59, (1955), 7
- [15] W. Baumann, H. Gg. Wagner: "Einfluss der Frischgasströmung auf die Beschleunigung von Flammen und den Anlaufvorgang von Detonationen". Z. Elektrochem. 65, (1961), 895
- [16] D. H. Edwards, D. J. Larry: "Wave Front Structure in Spinning Detonation"; J. Fluid Mechanics 26, (1966), 321
- [17] W. Busch, H. Gg. Wagner: "Investigation of the Dependence of Limits of Detonability on Tube Diameter"; Comb. Flame 6, (1962), 157
- [18] W. Busch, H. Gg. Wagner: "Einfluss des Rohrdurchmessers auf die Ausbreitung einer Detonation in explosiblen Gasgemischen" Teil I: Inertgas- und Rohrdurchmessereinfluss auf die Detonationsgrenzen einiger explosibler Gasgemische"; Ber. Bunsenges. phys. Chem. 69, (1965), 503
- [19] K. Guhlmann, H. Gg. Wagner: Einfluss des Rohrdurchmessers auf die Ausbreitung einer Detonation in explosiblen Gasgemischen. Teil II: Einfluss des Ausgangsdruckes und des Rohrdurchmessers auf die Detonationsgrenzen der Systeme  $\text{CH}_4 - \text{O}_2 - \text{N}_2$  und  $\text{CH}_4 - \text{O}_2 - \text{Ar}$ ; Ber. Bunsenges. phys. Chem. 70, (1966), 143

GENERAL REFERENCES

- W. Jost: "Explosions- und Verbrennungsvorgänge in Gasen"; Springer, Berlin, 1939
- B. Lewis, G. von Elbe: "Combustion, Flames and Explosion of Gases"; Academic Press Inc., New York, London, 1961
- B. Zeldovich, A. S. Kompaneets: "Theory of Detonation"; Academic Press, New York, London, 1961
- R. Courant, K. Friedrichs: "Supersonic Flow and Shock Waves in Gases"; Interscience Publishers, Inc., New York 1948
- E. F. Greene, J. P. Toennies: "Chemische Reaktionen in Stoßwellen". Fortschritte der physikalischen Chemie, Darmstadt, 1959
- A. Van Tiggelen et.al.: "Oxydations et Combustions"; Tome II, Publications de l'Institut Français du Pétrole, Editions Technip, Paris, 1968
- A. S. Sokolik: "Self-Ignition, Flame and Detonation in Gases" Jerusalem 1963.

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13. ABSTRACT The influence of initial temperature on the limits of detonability of gaseous detonations is investigated for mixtures of $\text{CH}_4\text{-O}_2$ , $\text{H}_2\text{-O}_2$ , and $\text{H}_2$ -air at one atmosphere initial pressure in long tubes of 4, 6, 10, 16, and 26mm, inner diameter, respectively, by use of a rotating drum camera. Two experimental designs are described to measure these limits at low initial temperatures. The regime of fuel gas concentrations for stable detonations becomes somewhat narrower at lower initial temperatures. The influence of the initial temperature on the critical tube diameter is estimated. Furthermore the applicability of the Chapman-Jouguet theory is discussed in relation to shock wave configurations, i.e. the Mach triple configuration. The essential arguments for the existence of the limits of detonability are discussed. Finally a new method to estimate the limits of detonability with a very simple experimental arrangement is described. By this method experiments concerning the stability of a detonation and its initiation process are linked together.			

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	Limits of detonability						
	Chapman-Jouguet theory						
	Shock wave configurations						
	Critical tube diameter						
	Onset of a detonation						
	Tube length						

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